



## Effect of zirconia in the density and ionic conductivity properties of $\text{Bi}_4\text{V}_{1.8}\text{Cu}_{0.1}\text{Zn}_{0.1}\text{O}_{10.7}$ compound

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### Abstract

Ceramics based bismuth vanadate are conductors of oxygen ions and they are used as solid electrolytes in pressure sensors and fuel cells. These materials operate at temperatures above 700 °C. At high temperatures, the bismuth-vanadium oxide ( $\text{Bi}_4\text{V}_2\text{O}_{11}$ ) has a  $\gamma$ -phase with a large number of oxygen vacancies that favors the ionic conductivity. The  $\gamma$ -phase of the  $\text{Bi}_4\text{V}_2\text{O}_{11}$  was stabilized at room temperature by partial substitution of vanadium ( $\text{V}^{5+}$ ) ions by cuprum ( $\text{Cu}^{2+}$ ) and zinc ( $\text{Zn}^{2+}$ ) ions to provide high ionic conductivity values between 100 and 400°C. Thus, polycrystalline samples of  $\text{Bi}_4\text{V}_{1.8}\text{Cu}_{0.1}\text{Zn}_{0.1}\text{O}_{10.7}$  were obtained after 4h sintering at 800 °C. Investigations were made about densification process and ionic conductivity related to the effect of addition of the yttria-stabilized zirconia ( $\text{Zr}_{0.88}\text{Y}_{0.12}\text{O}_{1.94}$ ).

**Keywords:** Bismuth-vanadium oxide, yttria-stabilized zirconia, oxygen ion conductor.

### Efecto de la zirconia en las propiedades densidad y conductividad iónica del compuesto $\text{Bi}_4\text{V}_{1.8}\text{Cu}_{0.1}\text{Zn}_{0.1}\text{O}_{10.7}$

### Resumen

Cerámicas de vanadato de bismuto son conductores de iones de oxígeno y se utilizan como electrolitos sólidos en los sensores de presión y pilas de combustible. Estos materiales funcionan a temperaturas superiores a 700 °C. A altas temperaturas, el óxido de bismuto-vanadio ( $\text{Bi}_4\text{V}_2\text{O}_{11}$ ) tiene una fase- $\gamma$  con un gran número de vacantes de oxígeno que favorece la conductividad iónica. La fase- $\gamma$  del  $\text{Bi}_4\text{V}_2\text{O}_{11}$  fue estabilizado a temperatura ambiente por sustitución parcial de iones de vanadio ( $\text{V}^{5+}$ ) por iones de cobre ( $\text{Cu}^{2+}$ ) y iones de zinc ( $\text{Zn}^{2+}$ ) para proporcionar valores de conductividad iónica alta entre 100°C y 400°C. Por lo tanto, las muestras policristalinas de  $\text{Bi}_4\text{V}_{1.8}\text{Cu}_{0.1}\text{Zn}_{0.1}\text{O}_{10.7}$  se obtuvieron después de la sinterizarlas durante 4 horas a 800°C. Se estudió el proceso de densificación y la conductividad



28

iónica relacionada con el efecto de la adición de la zirconia estabilizada con itria ( $\text{Zr}_{0.88}\text{Y}_{0.12}\text{O}_{1.94}$ ).

**Palabras clave:** Óxido de Bismuto-Vanadio, zirconia estabilizada con itria, conductor de iones de oxígeno.

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## Introduction

The  $\text{Bi}_4\text{V}_2\text{O}_{11}$  has a  $\gamma$ -phase at high temperature (700 °C) that exhibits a relatively high conductivity when compared to others conventional ionic conductors, as  $\text{CeO}_2$  and  $\text{ZrO}_2$ . Partial substitutions of metal ions, such as ions of Cu, Ni, Zn, etc., by vanadium can stabilize the  $\gamma$ -phase of the  $\text{Bi}_4\text{V}_2\text{O}_{11}$  at room temperature and they have been found to result in materials exhibiting high ionic conductivities<sup>1,2,3,4</sup>. Thus, the materials of the called BIMEVOX family are considerably attractive to use in ionic conductors at low temperatures (300 to 400 °C); to applications as oxygen gas sensors.

On this work, the  $\gamma$ -phase of the  $\text{Bi}_4\text{V}_2\text{O}_{11}$  was stabilized at low temperature by substitutions of  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  ions by  $\text{V}^{5+}$  ions in molar fraction of 5%. These partial substitutions formatted the  $\text{Bi}_4\text{V}_{1.8}\text{Cu}_{0.1}\text{Zn}_{0.1}\text{O}_{10.7}$  compound which was sintered for 4h at 800 °C in format of ceramics pellet. In addition, the yttria-stabilized zirconia ( $\text{Zr}_{0.88}\text{Y}_{0.12}\text{O}_{1.94}$ ) was added to the doped bismuth-vanadium oxide in mass fraction of 5%, 10%, 15% and, 20%. Density measurements was made to verify the densification obtained of the material by the sintering process used in this work. The ionic conductivity investigation of the  $\gamma$ - $\text{Bi}_4\text{V}_{1.8}\text{Cu}_{0.1}\text{Zn}_{0.1}\text{O}_{10.7}$  with and

without  $\text{Zr}_{0.88}\text{Y}_{0.12}\text{O}_{1.94}$  was realized by impedance spectroscopy method.

## Experimental part

The commercial oxides used as basic substances to obtaining of  $\text{Bi}_4\text{V}_2\text{O}_{11}$  compound were: bismuth oxide ( $\text{Bi}_2\text{O}_3$ ) from Victoria Química-São Paulo/BR and vanadium oxide ( $\text{V}_2\text{O}_5$ ) from Vetec-Rio de Janeiro/BR. And the commercial oxides used as doping agents to obtaining of BICUZNVOX were: CuO from Mallinckrodt-Missouri/USA and ZnO from Merck. In addition, was used the commercial oxide of yttria-stabilized zirconia 12% in moll ( $\text{Zr}_{0.88}\text{Y}_{0.12}\text{O}_{1.94}$  or 12YSZ) from Toyo Soda to increasing the densification of the samples.

Samples were prepared by mixing appropriate proportions of the precursors oxides<sup>5</sup> and their compositions were established after an analysis of literature data observing<sup>1,2,6</sup> the compositions exhibit the best results of electrical and physics (density) properties. These compositions were specified as BICUZNVOX.10 for the  $\text{Bi}_2\text{V}_{0.9}\text{Cu}_{0.05}\text{Zn}_{0.05}\text{O}_{5.35}$  (or  $\text{Bi}_4\text{V}_{1.8}\text{Cu}_{0.1}\text{Zn}_{0.1}\text{O}_{10.7}$ ) sample and for samples of the  $\text{Bi}_2\text{V}_{0.9}\text{Cu}_{0.05}\text{Zn}_{0.05}\text{O}_{5.35}$  with addition of 5%, 10%, 15%, and 20% of zirconia mass fraction as being  $(\text{Cu}_{0.05}\text{Zn}_{0.05})_{1-x}(\text{12YSZ})_x$  with  $x = 0.05; 0.10; 0.15$  and  $0.20$ .

Polycrystalline samples of BICUZNVOX.10 in monolithic pellets

30

format were obtained by sintering for 4 h at 800 °C after a study of densification<sup>5</sup>. The sintering was made in the muffle EDGON 1P 1800 model. Likewise, for the investigation of the effect caused by addition of yttria-stabilized zirconia in the ionic conductivity and densification of the material, the samples of BICUZNVOX.10 with 12YSZ were sintered in the same temperature and time (at 800 °C for 4 h).

Electrical impedance measurements of pellets of the  $(\text{Cu}_{0.05}\text{Zn}_{0.05})_{1-x}(\text{12YSZ})_x$  and BICUZNVOX.10 were realized by Impedance Analyzer Hewlett Packard 4192A LF Model with the Impedance Measurements software using the appropriate input parameters<sup>[5]</sup>. It was used the frequency range of 5 to  $13 \times 10^6$  Hz and the temperature range of 100 to 400 °C with 50 °C increment. Data Analysis software was used to the inquiry of impedance values.

## Results and discussion

### Physics (density) characterization

The best results of densification for BICUZNVOX.10 were obtained at 800 °C for 4h of sintering. With these results was realized a study of the effect of yttria-stabilized zirconia (12YSZ) about the BICUZNVOX.10 compound densification to mass

fractions of 5%, 10%, 15% and 20% (see Figure 1).

The geometric density of the BICUZNVOX.10 increases with the increasing of zirconia quantity. Low variation was obtained in the correlation factor (Density vs Zirconia mass) of the sintered samples relative to samples not sintered (11.4754%). In other words, the increased density sintered samples in 5.1498% compared to the same non-sintered samples. This observation is a normal comportment similar to the values found in the literature<sup>7,8,9,10,11</sup>. Zirconium oxide, besides be an oxygen ion conductor, has a high refractory property so as does not react with the liquid phase formed in the BICUZNVOX.10 compound and it is responsible for the densification process.

### Electrical characterization

Impedance measurements results were used to verify the material behavior related to ionic conductivity. In the impedance spectroscopy diagrams, it was possible to observe two contributions present to conductivity process: by grain boundary and grain for some test temperatures. However, there is no possibility to discern both contributions in others temperatures of test. The total resistance of the specimens at different temperatures

31

was calculated from the point of intersection of the impedance spectrum with the real axis of the impedance spectroscopy diagram.

The results obtained of ionic conductivity showed a decreasing of impedance with the increasing of temperature (Figure 2(a) and 2(b)). This phenomenon is due to excitation of the charge carriers, ions, around of its equilibrium positions in the crystalline lattice.

The Arrhenius plots for the conductivity behavior of solid solution samples are shown in the Figure 3. This confirms the charge transport process is thermally activated. In addition, there was no significant difference between the activation energy values of the BICUZNVOX.10 samples with the increasing of zirconia quantity. Activation energy values in this work (approximately 0.26 eV) are smaller than literature's values found<sup>7,8</sup>. These values indicate, therefore, which the conduction mechanism is attributed predominantly by electrons hopping<sup>12</sup>.

It was also possible to analysis how the ionic conductivity behaved when the yttria-stabilized zirconia was added. Zirconium oxide has a high refractory property that increasing the density of the BICUZNVOX.10 but, it not exhibits a good conductivity at low

temperatures<sup>7</sup> and the ionic conductivity of bismuth vanadate oxide, therefore, not showed high values (Figure 4).

In this case, zirconia oxide behaves as impurity in the material to difficult the oxygen ions passage. However, these results of ionic conductivity obtained in this work are in good agreement with those found in the literature. Table 1 compare some ionic conductivity values with some of literature<sup>1,13,14,15,16</sup> at 300 °C.

## Conclusions

The  $\gamma$ -phase of  $\text{Bi}_4\text{V}_2\text{O}_{11}$  could be stabilized at room temperature by partial substitutions of  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  ions by  $\text{V}^{5+}$  ions. Thus, the effect caused by addition of yttria-stabilized zirconia,  $\text{Zr}_{0.88}\text{Y}_{0.12}\text{O}_{1.94}$ , was investigated in the densification process and ionic conductivity of the  $\text{Bi}_4\text{V}_{1.8}\text{Cu}_{0.1}\text{Zn}_{0.1}\text{O}_{10.7}$  samples. The yttria-stabilized zirconia does not react with the constituents oxides and permits the densification of the samples. However, the ionic conductivity decreases with the increasing of zirconia quantity. The activation energy not showed significative variation with the increasing of zirconia quantity. In addition, the samples with 12YSZ exhibited low activation energy values, about 0.26 eV.

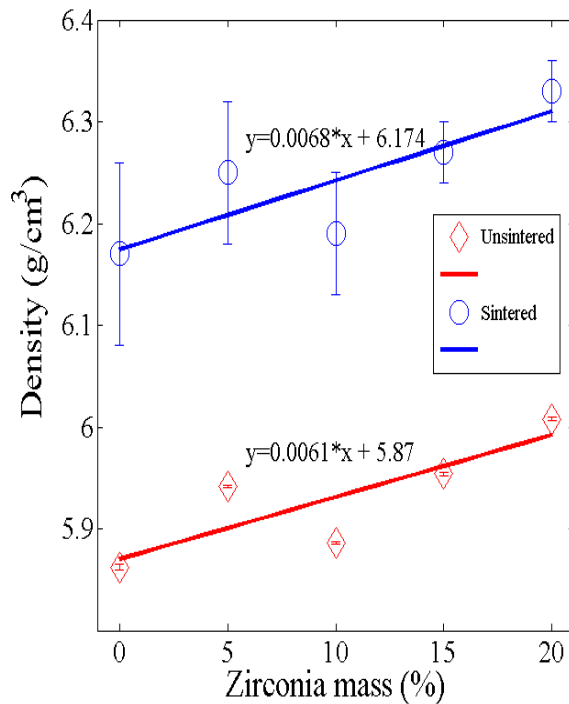


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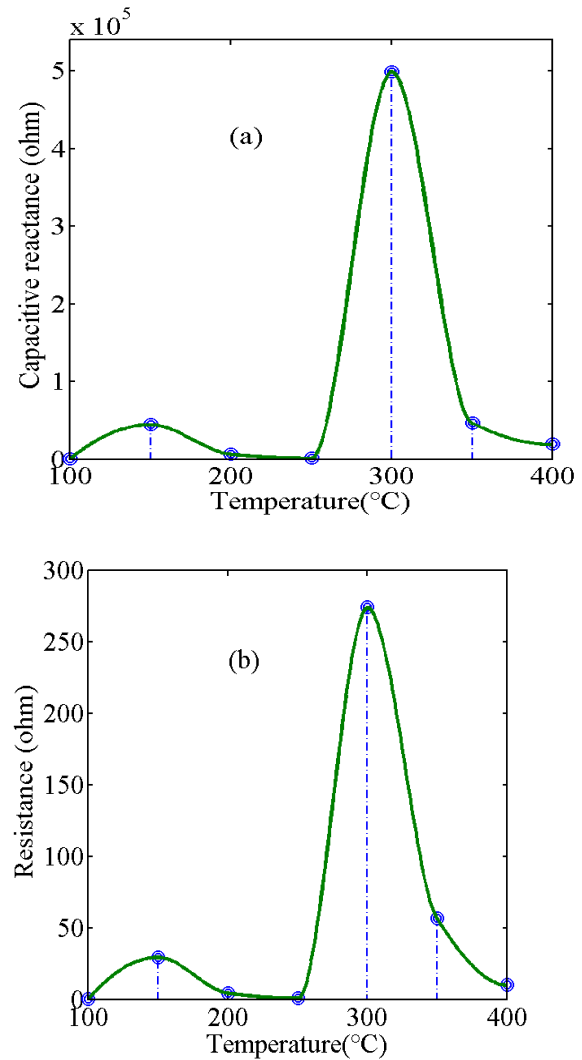
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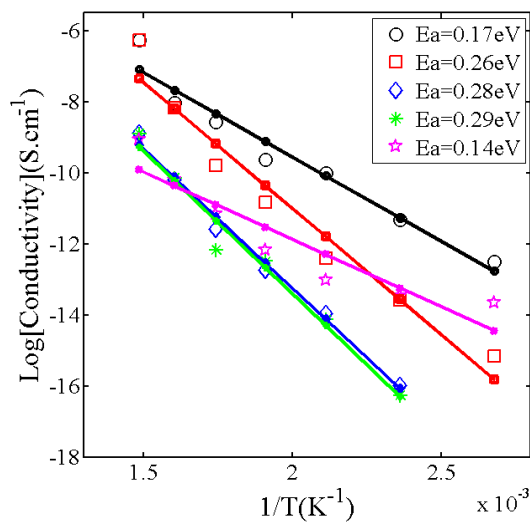


**Figure 1.** Densification behavior of the BICUZNVOX.10 material related to addition of  $Zr_{0.88}Y_{0.12}O_{1.94}$  (5%, 10%, 15% and 20%) to the samples sintered at 800 °C for 4h

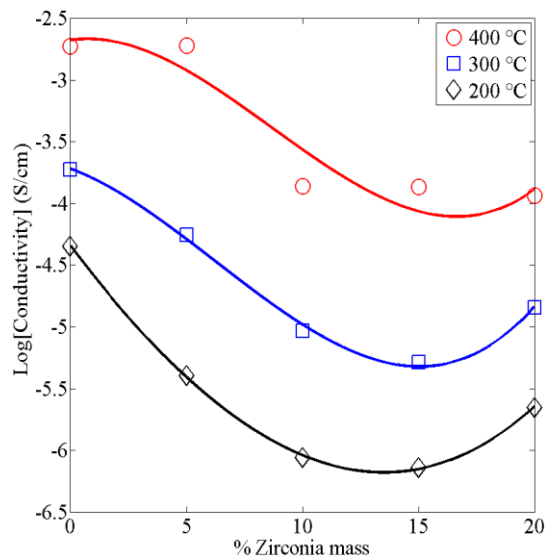


**Figure 2.** Behavior analyzes about electrical properties by temperature of the BICUZNVOX.10 samples: (a) capacitive reactance and (b) resistance.





**Figure 3.** Ionic conductivity of the BICUZNVOX.10 samples with: (○) 0%, (□) 5%, (◇) 10%, (●) 15%, and (⊙) 20% mass of yttria-stabilized zirconia sintered at 1073 K for 4h.



**Figure 4.** Ionic conductivity of BICUZNVOX.10 with addition of 12YSZ(0%, 5%, 10%, 15% and 20%) sintered at 800 °C for 4h.

**Table 1.** Ionic conductivity values for several solid electrolytes.

Samples	$\sigma$ (S/cm) at 300 °C
$\text{Bi}_2\text{V}_{0.90}\text{Cu}_{0.05}\text{Zn}_{0.05}\text{O}_{5.35}$ (*)	$1.88 \times 10^{-4}$
$(\text{Cu}_{0.05}\text{Zn}_{0.05})_{0.95}(\text{12YSZ})_{0.05}$ (*)	$5.56 \times 10^{-5}$
$(\text{Cu}_{0.05}\text{Zn}_{0.05})_{0.90}(\text{12YSZ})_{0.10}$ (*)	$9.33 \times 10^{-6}$
$(\text{Cu}_{0.05}\text{Zn}_{0.05})_{0.85}(\text{12YSZ})_{0.15}$ (*)	$5.15 \times 10^{-6}$
$(\text{Cu}_{0.05}\text{Zn}_{0.05})_{0.80}(\text{12YSZ})_{0.20}$ (*)	$1.43 \times 10^{-5}$
$\text{Bi}_2\text{V}_{0.90}\text{W}_{0.10}\text{O}_{5.35}$ [13]	$7.94 \times 10^{-5}$
$\text{Bi}_2\text{V}_{0.90}\text{Zr}_{0.10}\text{O}_{5.35}$ [14]	$6.30 \times 10^{-5}$
$\text{Bi}_2\text{V}_{0.90}\text{Cu}_{0.05}\text{Zn}_{0.05}\text{O}_{5.35}$ [11]	$3.16 \times 10^{-3}$
$\text{Bi}_2\text{V}_{0.90}\text{Cu}_{0.05}\text{Ni}_{0.05}\text{O}_{5.35}$ [11]	$2.51 \times 10^{-3}$
$\text{Bi}_2\text{V}_{0.90}\text{Ni}_{0.05}\text{Zn}_{0.05}\text{O}_{5.35}$ [11]	$1.78 \times 10^{-3}$
$\text{Bi}_2\text{V}_{0.90}\text{Cu}_{0.05}\text{Mo}_{0.05}\text{O}_{5.35}$ [11]	$1.33 \times 10^{-3}$
$\text{Bi}_2\text{V}_{0.90}\text{Cu}_{0.10}\text{O}_{5.35}$ [15]	$2.32 \times 10^{-3}$
$\text{Bi}_2\text{V}_{0.90}\text{Mg}_{0.10}\text{O}_{5.35}$ [16]	$1.10 \times 10^{-3}$

\* Values found in this work.

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